ALKYLATING PROPERTIES OF ALKYL PERFLUOROISOBUTENYL ETHERS COMMUNICATION 2. REARRANGEMENT OF ALKYL PERFLUOROISOBUTENYL ETHERS TO ACID FLUORIDES OF α -ALKYLHEXAFLUOROISOBUTYRIC ACIDS*

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Alkyl perfluoroisobutenyl ethers (I) possess alkylating properties, and adducts (II) are formed when they are reacted with trialkylamines [1, 2]. The obtained adducts are easily alkylated at the α -carbon atom, being converted to the acid fluorides of α -alkylhexafluoroisobutyric acids (III) [1].



It could be expected that under certain conditions the adducts (II) will be alkylated not only by alkyl iodides, but also by the starting ethers (I). Actually, the acid fluoride of α -ethylhexafluoroisobutyric acid (IIIb) \dagger is formed when a mixture of equimolar amounts of adduct (IIa) and ethyl perfluoroisobutenyl ether (Ib) is heated.



Since adduct (IIa) is regenerated here, the reaction should go even in the presence of catalytic amounts of this adduct. Together with this, the (II) adducts are formed from alkyl perfluoroisobutenyl ethers and

*See [1] for previous communication.

†The acid fluoride of α -methylhexafluoroisobutyric acid (IIIa) was not detected in the reaction products, which excludes the possibility of forming acid fluoride (III) via transfer of alkyl from the nitrogen atom in adduct (II).

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trialkylamines even at room temperature [1, 2], so that in the final analysis the reaction can be reduced simply to the rearrangement of the alkyl perfluoroisobutenyl ether (I) to the acid fluoride of the α -alkylhexafluoroisobutyric acid (III) when the reaction mixture is heated in the presence of catalytic amounts of the trialkylamine. Actually, the heating of ethers (I) with a small amount of triethylamine leads to the formation of the acid fluorides (III).*



Ethyl ether (Ib) is rearranged under more drastic conditions than is methyl ether (Ia), which is evidently due to steric hindrance. In the absence of the tertiary amine the methyl ether (Ia) does not rearrange even at 180°, whereas in the presence of triethylamine the rearrangement is noticeable even at 20°C. † Usually the rearrangement of alkyl vinyl ethers to C-alkylated carbonyl compounds is accomplished under drastic conditions, for example, by heating at 200-300° in the presence of catalysts (Al₂O₃, SiO₂, etc.) [5]. These reactions are frequently accelerated in the presence of radical initiators [5-7]. Allyl vinyl ethers undergo rearrangement (Claisen rearrangement) more easily than do alkyl vinyl ethers. Allyl perfluoroisobutenyl ether (Ic) is rearranged under unusually mild conditions even at the moment of formation to the acid fluoride of α -allylhexafluoroisobutyric acid (IIIc); the preparation of ester (IV) from perfluoroisobutylene (V) and allyl alcohol is explained in specifically the same manner [8].



In the same paper [8] is described some other cases of facile Claisen rearrangement for allyl vinyl ethers that have fluorine-containing substituents in the vinyl group. It could be expected that a similar rearrangement will go when tetrakis(trifluoromethyl)allene (VI) is reacted with allyl alcohol. Actually, the allyl ether of the enol (VII) that is formed here is easily rearranged to the corresponding allyl ketone (VIII).



The intermediate formation of ether (VII) was proved by means of the F^{19} NMR spectra (Fig. 1). As a result, in the Claisen rearrangement, the same as in the rearrangement of alkyl perfluoroisobutenyl ethers, fluorine-containing substituents in the vinyl group make the reaction go more easily in that they facilitate rupture of the allyl – oxygen (or correspondingly alkyl – oxygen) bond. In this connection the rearrangement of allyl vinyl ethers of the (Ic) or (VII) type does not require catalysts, since the nucleophilicity of the central carbon atom of the perfluoroisobutenyl group is sufficient for its intramolecular alkylation. In the case of alkyl perfluoroisobutenyl ethers (Ia, b) the direct intramolecular rearrangement is difficult, since the corresponding transition state is much less favorable. \ddagger

^{*}See [3] for the preliminary communication on this reaction.

[†]Ether (Ia) decomposes when heated at 400° with the formation of bis(trifluoromethyl)ketene and the acid fluoride of α -hydrohexafluoroisobutyric acid [4].

[‡]A four-membered cyclic transition state is postulated as being one of the possible variations in the rearrangement of trifluoromethyl trifluorovinyl ether to the acid fluoride of perfluoropropionic acid under very drastic conditions (595°) [9].





However, during the transformation of the alkyl perfluoroisobutenyl ethers (Ia, b) to the (II) adducts the nucleophilicity of the central carbon atom is increased sharply and it now becomes possible to effect alkylation using various alkylating agents, including ethers (Ia, b) themselves. The rearrangement of alkyl perfluoroisobutenyl ethers is a convenient method for the preparation of the acid fluorides of α -alkylhexafluoroisobutyric acids (III),* which, in turn, can serve as intermediates in the synthesis of other organofluorine compounds. Thus, the salts of α -alkylhexafluoroisobutyric acids (IX), easily formed by the hydrolysis of acid fluorides (III), are converted when heated to 2-alkylpentafluoropropylenes (X).

^{*}Previously acid fluorides (IIIa, b) were obtained by the alkylation of the adduct of the acid fluoride of hexa-fluoroisobutyric acid and triethylamine [10, 11].



In this way were obtained the difficultly accessible 2-methylpentafluoropropylene (Xa) and the previously unknown 2-ethylpentafluoropropylene (Xb).

It is interesting that the rate of reaction of acid fluorides (IIIa, b) with nucleophilic reagents is determined by steric hindrance. Thus, in order to obtain the ethyl ester of α -ethylhexafluoroisobutyric acid (XI) it is necessary to reflux the ethyl-substituted acid fluoride (IIIb) with alcohol.



At the same time, the methyl-substituted acid fluoride (IIIa) reacts easily with alcohol even at room temperature.

EXPERIMENTAL

The NMR spectra were taken on a Perkin-Elmer R-12 spectrometer using hexamethyldisiloxane as the internal standard. The F^{19} NMR spectra were taken on a Hitachi spectrometer (operating frequency 56.46 MHz) using CF₃COOH as the external standard. The chemical shifts are given in parts per million (ppm) from (CH₃)₄Si or CF₃COOH, respectively.

Acid Fluoride of α -Methylhexafluoroisobutyric Acid (IIIa). To 5 g of methyl perfluoroisobutenyl ether (Ia) was added six drops of absolute $(C_2H_5)_3N$ and the obtained mixture was heated in a sealed ampul on the boiling water bath for 10 h. The ampul was opened, another two drops of absolute $(C_2H_5)_3N$ was added, and the mixture was heated in a sealed ampul for another 23 h. Distillation gave 4.2 g (84% of theory) of (IIIa) with bp 47-49°C. From [10]: mp 47-47.5° (753 mm). NMR spectrum: δ_{CH_3} 1.81 (singlet). F¹⁹ NMR spectrum: -6.7 (CF₃, doublet), -118 (COF, heptet), J_{F-F} 9.7 Hz.

The treatment of (IIIa) with methanol gave an ester that was chromatographically identical with an authentic sample of the methyl ester of α -methylhexafluoroisobutyric acid [12]. From (IIIa) and C₆H₅NH₂ in ether solution was obtained the anilide of α -methylhexafluoroisobutyric acid, yield 79% of theory, mp 60-65°. The mixed melting point with an authentic sample was not depressed. From [10]: mp 67°.

The rearrangement of ether (Ia) to (IIIa) in tetrahydrofuran (THF), in the presence of $(C_2H_5)_3N$, becomes noticeable even at 20° (NMR spectra). However, in the absence of $(C_2H_5)_3N$, ether (Ia) remains unchanged even when heated in a sealed ampul at 180°.

Acid Fluoride of α -Ethylhexafluoroisobutyric Acid (IIIb). A mixture of 28.3 g of ethyl perfluoroisobutenyl ether (Ib) and approximately 1 ml of absolute $(C_2H_5)_3N$ was heated in a sealed ampul for 22 h at 150°. Distillation gave 23.9 g (84%) of (IIIb) with bp 73-75° and n_D^{18} 1.3082. From [11]: mp 75-76.5° (755 mm); n_D^{20} 1.3049. F¹⁹ NMR spectrum: -10.3 (CF₃, doublet), -111 (COF, heptet), J_F - F 10.5 Hz.

A mixture of 3.24 g of adduct (Ia) with $(C_2H_5)_3N$ (IIa) [1] and 2.69 g of (Ib) was heated in a sealed ampul for 18 h at 120°, and for 15 h at 145°. The volatile products were evaporated in a vacuum system and condensed in a trap, cooled in liquid nitrogen. We obtained 2.47 g (92%) of acid fluoride (IIIb) with bp 76-78°, which was chromatographically identical with an authentic specimen. Based on the GLC data, the product is practically devoid of (IIIa).

Into 8.12 g of (Ib) was passed a small amount of anhydrous $(CH_3)_3N$, in which connection a precipitate was obtained. The mixture was refluxed for approximately 1.5 h, in which connection rearrangement was not observed (the boiling point of the liquid (113-114°) failed to drop). A sufficient amount of absolute CH_3CN was added so that the reflux temperature of the mixture was 100°. The mixture was refluxed for 9 h; here the boiling point of the liquid dropped to 88°. Several drops of absolute $(C_2H_5)_3N$ were added, and the mixture was refluxed for another 17 h (the reflux temperature of the liquid dropped to 82°). From the mixture was distilled 3.64 g of crude (IIIb) with bp 73-90°. Based on the data of the NMR spectra, the product contains CH_3CN and the starting ether (Ib). From the crude acid fluoride (IIIb) and aniline was obtained the anilide of α -ethylhexafluoroisobutyric acid, mp 51-56°. NMR spectrum: δ_{CH_3} 1.11 (triplet), δ_{CH_2} 2.31 (quadruplet), $\delta_{C_6H_8} \sim 7.5$ (multiplet), $J_{CH_3} - CH_2$ 7.5 Hz. F¹⁹ NMR spectrum: -13.3 (CF₃, singlet). Based on the TLC data (in a mixture of acetone and hexane on Al₂O₃) the product is contaminated with the anilide of α -hydrohexafluoroisobutyric acid.

 $\frac{1-\text{Allyl-1,1,3,3-tetrakis(trifluoromethyl)acetone (VIII)}}{\text{II3} and 0.7 g of allyl alcohol was refluxed for 1.5 h (the temperature of the boiling liquid gradually rose from 50 up to 100°). Then the mixture was heated on the boiling water bath for 1 h, cooled, washed with water, and dried over CaCl₂. Distillation gave 2.56 g (71%) of ketone (VIII) with bp 133-135° and <math>n_{19}^{19}$ 1.3313. Found: C 32.52; H 1.66; F 60.64%. C₁₀H₆F₁₂O. Calculated: C 32.43; H 1.62; F 61.62%. Infrared spectrum: 1643 cm⁻¹ (C = C), 1750 cm⁻¹ (C = O). NMR spectrum: δ_{CH_2} 2.99 (broad doublet), $\delta_{(CF_3)_2CH}$ 4.77 (heptet), $\delta_{CH_2} = CH$ 5-6 (broad multiplet), $J_{CH_2} - CH$ 6.7 Hz. F¹⁹ NMR spectrum: -13.6 (FD, broad heptet), -15.0 (FE, doublet of heptets), $J_{FD} - F_E$ 3.3 Hz, $J_{FE} - H$ 6.5 Hz.

A mixture of (VI) and excess allyl alcohol in absolute ether was placed in an ampul for taking NMR spectra, and the sealed ampul was heated at 36° for 20 min. In the mixture was detected the addition product, namely the allyl ether of 1,1,1,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)-2-penten-3-ol (VII). F^{19} NMR spectrum: -22.3 (F_A, quadruplet of heptets), -19.4 (F_B, quadruplet), -14.3 (F_C, doublet of quadruplets), $J_{FA} - F_B$ 9.0 Hz, $J_{FA} - F_C$ 1.7 Hz, $J_{FC} - H$ 7.0 Hz. The mixture also contains ketone (VIII) (about 10%) and is devoid of the starting allene (VI) (see Fig.1a). On subsequent heating the amount of ketone (VIII) increased up to approximately 30% (after 0.5 h at 38-40°) and then up to approximately 60% (after another 1.5 h at 40-48°) (see Fig.1b). On further heating of the mixture (1.5 h at 65-72°) practically all of the enol ether (VII) was converted to ketone (VIII) (see Fig.1c).

Ethyl Ester of α -Ethylhexafluoroisobutyric Acid (XI). A mixture of 2.9 g of (IIIb) and 9 g of absolute alcohol was refluxed for 7 h, poured into water, and the organic layer was washed with water and dried over fused CaCl₂. Distillation gave 1.77 g (55%) of ester (XI), bp 134-140°; 67.3-68.0° (72 mm); n¹⁸_D 1.3440. From [11]: bp 63-64° (70 mm); n²⁰_D 1.3433. NMR spectrum: α -ethyl group, δ_{CH_3} 1.16 (triplet), δ_{CH_2} 2.25 (quadruplet), J_{H-H} 8.0 Hz; ethoxy group, δ_{CH_3} 1.38 (triplet), δ_{CH_2} 4.31 (quadruplet), J_{H-H} 6.6 Hz. F¹⁹ NMR spectrum: -10.7 (CF₃, singlet).

Acid fluoride (IIIb) reacts slowly with alcohol at room temperature: after approximately 20 h. The starting acid fluoride was detected by GLC; however, after 10 days the acid fluoride is converted entirely to ester (XI).

Acid fluoride (IIIa) reacts with alcohol at room temperature almost entirely in 10 min.

<u> α -Methylhexafluoroisobutyric Acid.</u> A mixture of 5.53 g of acid fluoride (IIIa), 3 g of KOH and 14 ml of water was kept at room temperature for 6 days, with periodic shaking. The solution was acidified with dilute HCl solution (1:5), extracted with ether, and the ether layer was dried over MgSO₄, after which the ether was distilled off. The residue represented 4.32 g (78%) of crude α -methylhexafluoroisobutyric acid, which was obtained as hygroscopic crystals. Acid equivalent: found 214, calculated for C₄H₃F₆COOH 210.

From 4.29 g of α -methylhexafluoroisobutyric acid and 1.84 g of aniline in 7 ml of benzene was obtained 5.13 g (85%) of the anilinium salt of α -methylhexafluoroisobutyric acid, mp 126-130° (from dichloroethane). Found: N 4.62; F 37.50%. C₁₁H₁₁F₆NO₂. Calculated: N 4.62; F 37.62%. F¹⁹ NMR spectrum: -9.2 (CF₃, singlet).

 $\frac{2-\text{Methylpentafluoropropylene (Xa)}. A \text{ mixture of 5.4 g of acid fluoride (IIIa), 15 ml of water and} 2.04 g of NaOH was shaken at periodic intervals for 3 h at room temperature until homogeneous. The solution was evaporated in vacuo. The residue represented 6.27 g of a mixture of NaF and the sodium salt of <math display="inline">\alpha$ -methylhexafluoroisobutyric acid. The mixture of salts was suspended in 20 ml of absolute $C_{6}H_{5}NO_{2}$, followed by stirring at 95-100°.* In a trap, cooled in a mixture of solid CO₂ and acetone, was collected 1.75 g (47%) of olefin (Xa), bp ~15°. From [14]: bp 12-13°. NMR spectrum: $\delta_{CH_{3}}$ 1.71 (doublet of doublets), $J_{CH_{3}} - F_{A}$ 3.1 Hz, $J_{CH_{3}} - F_{B}$ 3.2 Hz. F¹⁹ NMR spectrum: +7.5 (FA, doublet of quadruplets of quadruplets), +3.1 (FB, doublet of quadruplets of quadruplets), -13.0 (CF₃, doublet of doublets), $J_{FA} - F_{B}$ 28.6 Hz, $J_{FA} - CF_{3}$ 10.6 Hz, $J_{FA} - CH_{3}$ 3.1 Hz, $J_{FB} - CF_{3}$ 22.8 Hz, $J_{FB} - CH_{3}$ 3.2 Hz.

^{*}The corresponding potassium salt decomposes even at 80-85°.

<u>2-Ethylpentafluoropropylene (Xb)</u>. A mixture of 7.83 g of acid fluoride (IIIb), 20 ml of water and 3.88 g of KOH was shaken at periodic intervals for 5 days at room temperature until homogeneous. The solution was acidified with dilute HCl solution to approximately pH 2, extracted with ether, and the extract was dried over MgSO₄ and evaporated. The residue represented 6.9 g (89%) of crude α -ethylhexafluoroisobutyric acid, which was obtained as an oily liquid. Acid equivalent: found 230, calculated for C₅H₅F₆COOH 224. The obtained acid was treated cautiously with a solution of 2.9 g of KHCO₃ in 15 ml of water, and the resultant solution was evaporated in vacuo. The residue represented 7.19 g (89%) of the potassium salt of α -ethylhexafluoroisobutyric acid.

A suspension of 7 g of the obtained potassium salt in 15 ml of absolute $C_{6}H_{5}NO_{2}$ was heated, with vigorous stirring, at 100-110°. In a trap, cooled in a mixture of solid CO_{2} and acetone, was collected 2.16 g (51%) of (Xb), bp 33°. Found: C 37.38; H 3.06; F 59.63%. $C_{5}H_{5}F_{5}$. Calculated: C 37.50; H 3.12; F 59.37%. NMR spectrum: $\delta_{CH_{3}}$ 1.04 (triplet), $\delta_{CH_{2}}$ 2.16 (quadruplet of triplets), $J_{CH_{3}} - CH_{2}$ 7.7 Hz, $J_{CH_{2}} - F_{A}$ and $J_{CH_{2}} - F_{B} \sim 2.3$ Hz. F¹⁹ NMR spectrum: +8.3 (F_A, doublet of quadruplets of triplets), +2.7 (F_B, doublet of quadruplets of triplets), -15.2 (CF₃, doublet of doublets), $J_{FA} - F_{B}$ ^{27.6} Hz, $J_{FA} - CF_{3}$ ^{10.8} Hz, $J_{FB} - CF_{3}$ ^{22.4} Hz, $J_{FA} - CH_{2}$ and $J_{FB} - CH_{2} \sim 2.3$ Hz.

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CONCLUSIONS

1. Alkyl perfluoroisobutenyl ethers in the presence of catalytic amounts of tertiary amines are easily rearranged to the acid fluorides of α -alkylhexafluoroisobutyric acids. The mechanism of the reaction includes intermolecular alkylation of the mesomeric anion of the perfluoroisobutenolate by the action of the alkyl perfluoroisobutenyl ether.

2. When tetrakis(trifluoromethyl)allene is reacted with allyl alcohol the addition product, namely the allyl ether of the enol is formed initially, which, in the absence of catalyst, easily rearranges to 1-allyl-1,1,3,3-tetrakis(trifluoromethyl)acetone.

3. The acid fluorides of the α -alkylhexafluoroisobutyric acids were used as the starting materials for the preparation of 2-alkylpentafluoropropylenes.

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